

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Powder-Containing Preparations for Application to the Human Skin.

We, THE PERMUTIT COMPANY LIMITED, a British Company, of Permutit House, Gunnersbury Avenue, London, W.4, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Preparations for application to the human skin are of the most diverse formulations, but the vast majority contain powder, that is to say, very small solid particles. A preparation may contain more than one kind of powder, and the total amount of powder in a preparation may range from 95% or more by weight in face powders and baby powders to as little as 1% or 2% in cleansing creams and vanishing creams.

Some of the powders, for example precipitated chalk or zinc oxide, are included to give opacity. Most preparations contain a powder which acts essentially as a filler or a carrier for perfume or organic colouring matter, and this powder is most commonly talc, though it may be kaolin or chemically modified kaolin.

Talc and other filler powders are finely ground to give the impression of smoothness. The particle size is made so small that jagged edges are not felt. In a typical face powder, the average particle size is about 10 microns; the largest particles are about 65 microns, and the smallest particles optically resolved are about 3 microns in diameter. However, none of these powders can be ground to particles which are themselves completely smooth. Talc, for instance, may show a smooth crystal fracture in two dimensions, while having jagged edges in the third dimension. Finely ground

silk, sometimes used as a filler powder, is only smooth parallel to the fibre axis.

It is possible to produce polymer particles by the standard techniques of suspension polymerisation in the form of perfect spheres. The diameter of the polymer beads can be controlled by altering the conditions of the polymerisation such as the rate of stirring, the temperature of the suspension, the catalyst concentration, the pH, and the ratio of monomers to suspension medium. The average diameter may be made very low indeed, i.e. less than 100 microns. Since they are perfect spheres, such small polymer beads, which will be called micro-beads, are intrinsically "smooth" and do not merely feel smooth because of their small size.

The essence of this invention is the use of polymer micro-beads having an average diameter between 1 and 100 microns as a constituent of a powder-containing preparation for application to the human skin. By way of specific example, polymer micro-beads can replace talc (or the equivalent of talc) in any cosmetic preparation. The proportion of the micro-beads in a preparation according to the invention is from 5 to 95% by weight of the powder particles.

It is not feasible to produce micro-beads for use in the invention having an average diameter of much less than 5 microns, while the suitability of the beads for use in the preparations decreases if their average diameter is much above 60 microns. Preferably the beads have an average diameter between 3 and 100 microns and most preferably between 5 and 40 microns.

The advantage of increased smoothness is of course best obtained when the proportion

of polymer micro-beads in a preparation is high, and in general this proportion is at least 25% by weight in face powder and similar cosmetic powders.

- 5 The polymer micro-beads used in cosmetic preparations according to the invention are preferably cross-linked polymers, and most preferably cross-linked vinyl polymers, produced by the suspension polymerisation of a mixture of at least one monomer containing one polymerisable double bond and at least one monomer containing two or more double bonds, in the presence of a catalyst. Micro-beads of such copolymers are infusible and insoluble in all solvents, and thus capable of separation from monomers and other material to a very high degree of purity. However linear polymers which can be prepared as micro-beads of the correct particle size and with other suitable properties may be used. The micro-beads are unaffected by other constituents of the cosmetic preparations, and by anything with which they may come into contact in normal use of a cosmetic preparation.

- 30 For the manufacture of cross-linked resins, suitable monomers containing one polymerisable double bond include styrene, vinyl toluene, the esters of acrylic and methacrylic acids, e.g. methyl, ethyl and butyl esters, and vinyl acetate. Suitable monomers containing two or more polymerisable

double bonds include divinyl benzene, ethylene glycol diacrylate, ethylene glycol dimethacrylate, divinyl ketone and divinyl oxalate. Suitable catalysts are those yielding free radicals on heating and include benzene peroxide, lauroyl peroxide, acetyl peroxide, cumene hydroperoxide, and azo-bis-isobutyronitrile.

By suitable choice of the monomers, the characteristics such as the hydrophobic or hydrophilic properties or the natural, amphoteric or buffering properties of the micro-beads can be controlled. A simple cross-linked hydrocarbon micro-bead may, for example, be generally of a hydrophobic character and otherwise lacking in chemical properties; that is to say it may be non-polar and neither acidic nor basic. However, these properties may be modified by the incorporation of small percentages of other monomers during the production of the polymer micro-beads.

To illustrate this control of properties some examples of micro-bead polymers based on polystyrene cross-linked with divinyl-benzene (d.v.b.) and containing other monomers are given in the following table, together with some of their properties. The simple cross-linked hydrocarbon polymer is also included for comparison. All percentages and parts given in this specification are by weight unless otherwise stated.

		Composition (% by wt)			Properties
5	A.	Styrene	...	96	Inert and hydrophobic
		d.v.b.	...	4	
	B.	Styrene	...	95	Inert but less hydrophobic
		d.v.b.	...	4	
		hydroxyethyl acrylate	...	1	
10	C.	Styrene	...	86	Definitely hydrophilic
		d.v.b.	...	4	
		hydroxyethyl acrylate	...	10	
15	D.	Styrene	...	93	Mildly acidic (and hydrophylic)
		d.v.b.	...	4	
		methacrylic acid	...	3	
20	E.	Styrene	...	92	Mildly basic (and hydrophylic)
		d.v.b.	...	4	
		acrylate ester of an ethanolamine	...	4	
25	F.	Styrene	...	88	Neutral or amphoteric
		d.v.b.	...	4	
		methacrylic acid and acrylate ester of an ethanolamine in equivalent proportions	...	8	
30	G.	Styrene	...	90	More polar than A. Neutral but not of a buffering character like F.
		d.v.b.	...	4	
		acrylonitrile or acrylamide or ethylacrylate	...	6	

30 The copolymer of styrene, d.v.b. and hydroxyethyl acrylate is particularly attractive when hydrophilic properties are required.

35 Other suitable monomers or different combinations or both can be employed. For example the buffering effect of methacrylic acid and an amino-acrylate can be combined with the hydrophilic effect of hydroxyethyl acrylate or the contribution of an acrylate ester, such as ethyl acrylate, or acrylonitrile or acrylamide in increasing the polarity without increasing the number of actual acid or basic groups.

40 Cosmetic powders normally contain colouring matter in the form of particle of pigment. Polymer micro-beads can themselves be suitably coloured during their manufacture, and thus the need for a separate pigment in the powder can be obviated, if desired, though to obtain a suitable range of shades it may still be preferred to make the colouring matter a separate ingredient.

50 Examples of colouring matter that may be added are 2% iron oxide based on the weight of the microbeads, which can be mixed by grinding; dry Brilliant Green B.P., which can also be mixed by grinding in a proportion of 1% by weight of the micro-

beads to give a greenish-blue colour; and a 1% solution of Brilliant Green B.P. in water which can be added to the polymer beads with stirring in the proportion of 50% v/w to give a greenish blue colour.

Whiteness can be imparted by including titanium dioxide in the mixture that is polymerised or by so producing the beads by known methods that they have a very fine bubble structure and consequently are opaque.

70 The invention is useful in the first instance in cosmetic powders. Any conventional constituents of the powder should be finely ground, and from the point of view of smoothness should be as finely ground as possible, preferably to a particle size not exceeding 50 microns and advantageously less.

75 Various kinds of cosmetic powders in which the polymer micro-beads are advantageous will now be described.

80 The first is face powder. Face powders generally consist of a mixture of materials, both organic and inorganic. The usual organic materials are starches, such as rice or corn starch, Lycopodium powder and finely ground silk, and the common inor-

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 organic compounds include not only talc, but also zinc oxide, zinc carbonate and titanium dioxide. Surface-active agents, commonly metal soaps such as zinc or magnesium stearate, are usually incorporated to help the components of the powder to adhere to the skin surface. In addition to these materials, face powder usually contains colouring matter and perfume.

EXAMPLE 1

10 Polymer micro-beads were produced from a mixture of monomers consisting of 96% styrene and 4% d.v.b. by suspension polymerisation, the conditions being selected so
 15 that at least 95% of the micro-beads were between 3 and 15 microns in diameter. Such micro-beads are inert and hydrophobic. The beads were mixed with 5% of magnesium stearate, and the resultant mixture proved
 20 acceptable as a face powder in user trials.

EXAMPLE 2

Transparent and light face powder, designed to give bloom to the face, is of the following composition:—

25	Polymer beads (as used in Example 1)	...	80% by weight
	Rice starch	...	10% by weight
	Zinc oxide	...	5% by weight
	Zinc stearate	...	5% by weight

EXAMPLE 3

30 Face powder of high opacity is of the following composition:—

	Precipitated chalk	...	35% by weight
35	Polymer beads (as used in Example 1)	...	35% by weight
	Zinc oxide	...	25% by weight
	Zinc stearate	...	5% by weight

EXAMPLE 4

40 Baby powder which can be sterilised by heating for 1 hour in the temperature range of 150 to 160°C. consists of:—

	Polymer beads (as used in Example 1)	...	95% by weight
	Boric acid	...	5% by weight

EXAMPLE 5

45 Baby powder is of the following composition:—

	Polymer beads (as used in Example 1)	...	85% by weight
50	Corn starch	...	10% by weight
	Boric acid	...	5% by weight

55 Other cosmetic preparations according to this invention are essentially creams, in which it is an oil or solvent which is the essential ingredient and which is intended

to be brought into contact with the skin and to be spread on the skin to a limited extent. This is usually achieved by use of an aqueous emulsion so that the application of the oil is more controlled than if it were directly applied, when it would in most cases be applied too thickly. However, if the oil or other liquid is sufficiently stably emulsified for the product to be stable, there is so much emulsifying agent that the skin is excessively wetted with water, and the extent to which the desired liquid can come in contact with and coat or be absorbed into the skin is limited.

70 The cosmetic creams include cleansing preparations for the removal from the skin of oils or solvents or compositions containing oils or solvents. Such preparations usually consist essentially of an aqueous solution of a surface-active agent of adequate concentration, wetting power and emulsifying action. With these preparations the skin can be cleansed of the oil or other matter quickly and effectively but the skin may at the same time be degreased to an undesirable extent. If on the other hand a piece of soft material such as a cloth is used to wipe off the unwanted oil or solvent the process is slower and less effective though kinder to the skin.

85 Any such cream may advantageously include the polymer micro-beads as an aqueous dispersion, with or without a surface-active agent.

90 In preparations in which the primary object is to apply oil to the skin the micro-beads act as a carrier for the oil and thus such preparations consist essentially of an aqueous dispersion of oil-bearing micro-beads. Surface-active agents may be totally absent from the preparations or present in such small amounts that they do not interfere with the action of the preparation.

100 In preparations in which the primary object is to remove oil from the skin the beads may be dispersed in water without a surface-active agent or with a much smaller amount of a surface-active agent of a milder character than previously used. When this product is worked over the skin the oil is absorbed by the beads and the water is brought into direct contact with the skin, thus separating the latter from the material to be removed with much less drastic effects.

110 Micro-beads used in such oil-carrying or oil-removing preparations may advantageously have larger pores than polymer micro-beads produced by conventional methods.

115 Methods of producing microbeads with larger pores are known and include effecting the polymerisation of the monomers in a solvent which is either a precipitant or a swelling agent for the resultant copolymer, the monomers including a greater propor- 120

tion of cross-linking agent than in the conventional method. Such micro-beads may also be made by effecting the polymerisation in the presence of a polymeric substance that is completely soluble in (or miscible with) the monomer mixture to yield a single phase, and will not dissolve in or be dissolved by the resultant copolymer, and when the polymerisation has been effected removing the polymeric substance contained in the copolymer by solvent action, as described and claimed in our Application No. 36727/65 (Serial No. 1,140,910). Such beads are known as macroporous or macroreticular, and the large pores may suitably be from 300 to 10000 Angstroms units in size.

An example of a cosmetic cream according to this invention is as follows:—

EXAMPLE 6

Powder cream for combined creaming and powdering, or for skins with poor adhesion, is of the following composition:—

Polymer beads (of the same composition and average diameter as those in Example 1 but having pores of about 2000 Angstrom units size)	15% by weight
Glycerol monostearate	15% by weight
Glycerine	25% by weight
Water	45% by weight

If a copolymer is made as described in our Application No. 36727/65 (Serial No. 1,140,910) but the soluble polymeric substance it not leached out, the copolymer does not contain large void pores but has useful other properties. An example is a copolymeric substance produced by copolymerising 73.6% styrene, 6.4% d.v.b. in the presence of 20% polyisobutylene (of about 3000 molecular weight), the mixture also containing titanium dioxide in an amount equal to 20% by weight of the organic constituents. This substance has a waxy consistency and adheres well to the skin, so that it may advantageously be used in a powder.

Further cosmetic preparations in which micro-beads may be incorporated according to the invention are essentially greases, in that the base or major constituent is an oil, fat or wax. The viscosity of the base, or its consistency or rigidity, may not be suitable, and is commonly modified by the incorporation of materials soluble in the product. However such additives are now irrevocably present in the product, unless for example the oil is absorbed by the skin while the additive is not absorbed. Because of the sensitivity of human skin there is

always a risk that such additives may cause irritation, and if they are deposited within the pores they may subsequently absorb moisture and swell to block the pores.

The modification of the viscosity, consistency or hardness of the oil, fat or wax is effected, according to the invention, by the addition of the polymer micro-beads, which modify the bulk properties without altering the intrinsic properties of the continuous phase.

The viscosity of oils and greases, as measured under conditions of constant shear, increases approximately linearly with the proportion of micro-beads added. On the other hand the static viscosity, as measured by an adaptation of the falling ball method, of a grease is decreased. For example the viscosity of a grease composed of white soft paraffin to which 10% liquid paraffin has been added may be decreased by the addition of 10% micro-beads by weight. This combination of decreased static viscosity and increased viscosity under shear is beneficial in a cream as it is softer to scoop up on the fingers, but less fluid at the area of use. Other powder-containing preparations which may be applied to the skin include foot powder. An example of such a powder will now be given:—

EXAMPLE 7

Foot powder with fungicidal properties is of the following composition:—

Polymer beads (as used in Example 1)	70% by weight
Kaolin	10% by weight
Corn starch	15% by weight
Boric acid	2% by weight
Mixed t-butyl m- and p- cresols	2% by weight
Hexachlorophene	1% by weight

WHAT WE CLAIM IS:—

1. A powder-containing preparation for application to the human skin in which from 5 to 95% by weight of the powder particles are polymer micro-beads having an average diameter between 1 and 100 microns.
2. A preparation according to claim 1 in which the micro-beads are cross-linked polymers.
3. A preparation according to claim 2 in which the micro-beads are copolymers of styrene and divinyl benzene.
4. A preparation according to claim 2 in which the micro-beads are copolymers of styrene, divinyl benzene and hydroxyethyl acrylate.
5. A powder-containing preparation according to any one of claims 1 to 4 in which at least 5% of the powder particles are cross-linked polymer micro-beads of

average diameter between 3 and 100 microns, the powder also containing from 3 to 10% by weight of a metal soap.

- 5 6. A preparation according to any one of the preceding claims in the form of powder of which the polymer microbeads constitute at least 25% by weight.

- 10 7. A preparation according to any one of claims 1 to 5 in the form of cream in which the polymer micro-beads are present as an aqueous dispersion with or without a surface-active agent.

- 15 8. A preparation according to claim 7 in which the micro-beads are macroporous and have pores of from 300 to 10000 Angstrom units in size.

9. A preparation according to any of claims 1 to 5 in the form of grease.

10. A preparation according to any one of the preceding claims in which the polymer beads have an average diameter between 5 and 40 microns. 20

11. A preparation according to claim 1 substantially as described in any of the Examples herein. 25

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